Binuclear and polynuclear transition metal complexes with macrocyclic ligands

1. Synthesis and the structure of an antiferromagnetic binuclear nickel complex prepared by the reaction of *o*-phenylenediamine with pyrrole-2,5-dicarbaldehyde and nickel pivalate

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The reaction of pyrrole-2,5-dicarbaldehyde (**1**) with *o*-phenylenediamine (**2**) in anhydrous EtOH afforded a [1+1]-condensation product, *viz.*, Schiff's base. The structure of the latter was established by NMR spectroscopy and X-ray diffraction analysis. The reaction of this product or a mixture of **1** and **2** with $Ni_9(\mu_n\text{-}OOCBu^t)_{12}(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3$ in MeCN in the presence of AcOH gave rise to an antiferromagnetic binuclear complex. According to the X-ray diffraction data, the macrocycle in the latter complex is a [2+2]-condensation product of compounds **1** and **2**, μ_{eff} ranging from 0.569 to 2.614 μB (2—301 K), $-2J = 360\ cm^{-1}$. The $Ni_2(OAc)_2$ fragment is located in the central cavity of the macrocycle. The structures of the condensation products are discussed based on the results of DFT quantum-chemical calculations.

Key words: binuclear nickel(II) complexes, macrocyclic ligands, X-ray diffraction analysis, quantum-chemical calculations, DFT.

Transition metal complexes which contain two or several metal ions in the immediate vicinity of each other in the cavity of one macrocyclic ligand are of considerable interest as models of active centers of metal-containing proteins, molecular magnets, and potential components of homogeneous catalytic systems.[1—4] These complexes most commonly involve expanded porphyrins[5] or macrocyclic Schiff's bases as the ligands. The latter are prepared by [2+2]-condensation of α,α′-dicarbonyl derivatives of pyrroles, pyridines, α,α′-dipyrroles, or phenols with aromatic or aliphatic diamines. Homo- and heterobinuclear transition metal complexes with macrocyclic Schiff's bases based on 4-substituted 2,6-diformylphenols have been studied in sufficient detail.[6] However, complexes based on pyrrole-2,5-dicarbaldehyde (**1**) have received much less attention, direct reactions of compound **1** with aromatic diamines and its reactions in the presence of template agents being virtually unknown.

As part of our continuing studies on the synthesis and structures of polynuclear and binuclear transition metal complexes with macrocyclic ligands,[7] we examined the reaction of dialdehyde **1** with *o*-phenylenediamine (**2**) in the absence of template agents and also in the presence of the nonanuclear nickel complex $Ni_9(\mu_n\text{-}OOCBu^t)_{12}(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3$ (**3**).[8]

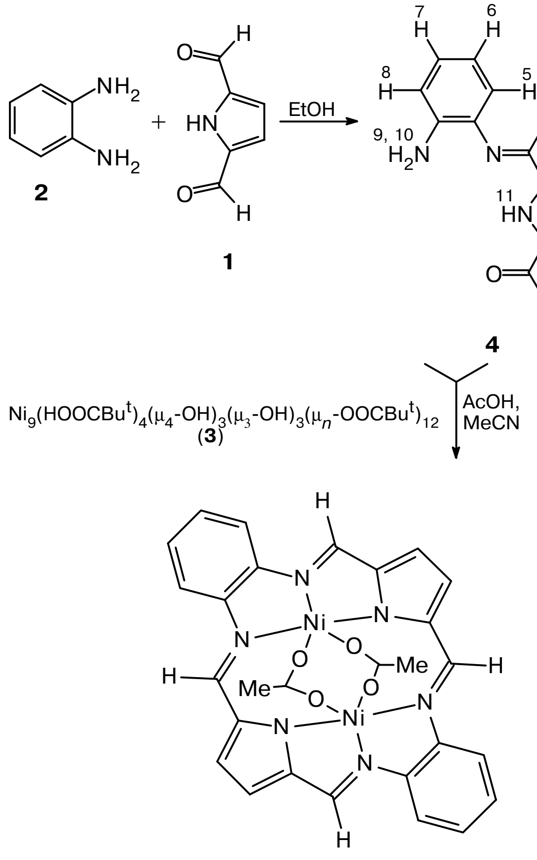
Results and Discussion

It is well known that dialdehyde **1** exists in solutions predominantly in the *cis-cis* conformation.[9] In this connection, the closure of the [2+2]-macrocycle would be expected to proceed readily in the absence of template agents. However, it appeared that the reaction of **1** with **2** in boiling ethanol (Scheme 1) afforded only rather inert Schiff's base **4** (yellow crystals), which did not undergo further condensation without additional activation. DFT quantum-chemical calculations,[10] which were carried out with the use of a program described previously,[11] demonstrated that the minimum of the total energy of molecule **4** corresponds to a non-planar conformation (the C(1)—C(6)—N(2)—C(7) torsion angle is 34.6°). The energy of another possible isomer in which the H atom is transferred from the pyrrole N atom to

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2334—2339, December, 2001.

the O atom of the formyl group is 19 kcal mol^{-1} higher. According to the results of calculations, compound **4** can form stable centrosymmetrical dimer **4**...**4** through four hydrogen bonds (the energy of dimerization is 15.4 kcal mol^{-1}).

Scheme 1



In a solution of compound **4** in DMSO, the H atom of the NH group of the pyrrole ring is involved in strong hydrogen bonding, which is unambiguously confirmed by its chemical shift (δ 12.5) in the ^1H NMR spectrum. Two protons of the NH_2 group give one substantially broadened signal at δ 5.60, which indicates that the rotation about the C—NH_2 bond is hindered.

According to the X-ray diffraction data, compound **4** actually exists as a dimer in the crystal (Fig. 1). Dimerization is realized through short hydrogen bonds between the O atoms of the aldehyde groups and the H atoms of the amino groups of the phenylene fragment and the NH group of the pyrrole ring (O(1)...H(NH), 2.157 Å; O(1)...H(NH_2), 2.328 Å).

It should be noted that the calculated geometric parameters of the dimer agree satisfactorily with the corresponding values obtained in the X-ray diffraction study. The bond lengths and bond angles have values typical of Schiff's bases characterized previously.[12] The dihedral angle between the planes of the pyrrole and phenyl rings is 18.3° (the calculated value is 14.3°). The plane passing through the atoms of the azomethine chain C(1)C(6)N(2)C(7) forms angles of 21.5 and 4.2° (the calculated values are 17.1° and 2.8°) with the planes of the phenyl and pyrrole rings, respectively. The formyl group is twisted about the C(4)—C(5) bond by 2.1° (the calculated value is 1.2°) out of the plane of the pyrrole ring. The molecule contains three protons (one proton at the N(1) atom of the pyrrole ring and two protons of the amino group at the N(3) atom) capable of hydrogen bonding. However, only two H atoms, *viz.* H(N(1)) and H(2N(3)), are involved in hydrogen bonds with the formyl O(1) atom to form H-bonded centrosymmetrical dimers **4**...**4**.

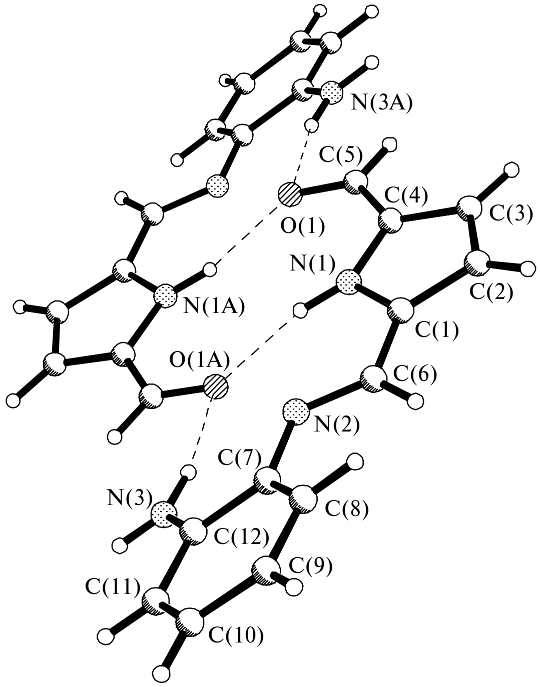
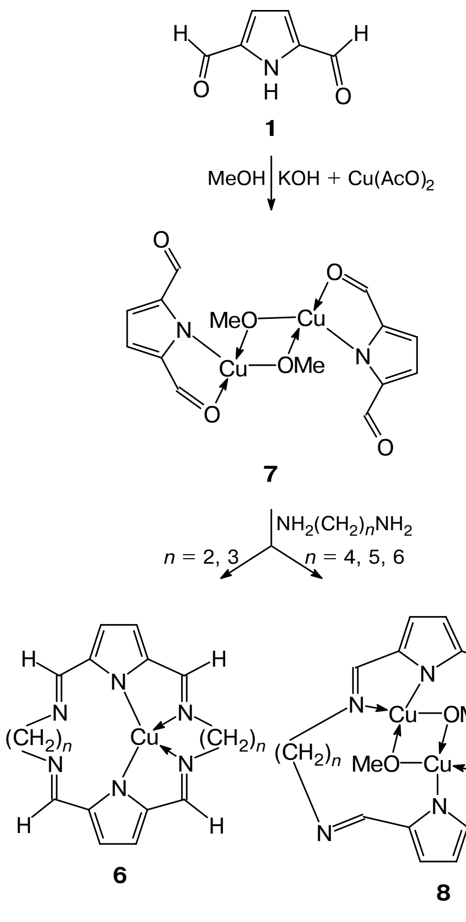


Fig. 1. Structure of the compound $C_{12}H_{11}N_3O$ (**4**).

Previously, it has been demonstrated that dialdehyde **1** reacts with aliphatic α,ω-diamines in the absence of metal ions to give oligo- and polycondensation products.[9,13] 1,2-Diaminoethane and 1,3-diaminopropan-2-ol are the exceptions; their reactions with compound **1** in the absence of template agents gave rise to macrocyclic Schiff's bases in rather high yields. The reaction of 3,4-diethylpyrrole-2,5-dicarbaldehyde with 1,2-diamino-4,5-dimethoxybenzene in the presence of strong acids (HNO_3 or HCl) afforded the [2+2]-macrocycle.[14]

Template syntheses based on dialdehyde **1** and diamines are generally carried out in the presence of deprotonating agents, an alkali, or 1,8-diamino-*N,N,N′N′*-tetramethylnaphthalene ("proton sponge").[13,14] Thus the reaction of copper acetate with compound **1** and 1,2-diaminoethane or 1,3-diaminopropane in methanol in the presence of KOH gave rise to mononuclear neutral complexes **6** (Scheme 2), which have been characterized by X-ray diffraction analysis. In these complexes, the copper atom in the cavity of the macrocycle is in a distorted planar-square environment and is bound to two pyrrole and two azomethine N atoms. Two other azomethine groups are not involved in coordination to the metal atom and this portion of the macrocycle is nonplanar. The reactions of α,ω-diamines $H_2N(CH_2)_nNH_2$ (n = 4—6) with binuclear copper alkoxide complexes **7** afforded homobinuclear complexes **8**. In these complexes, the $—Cu(OMe)_2Cu—$ fragment is located inside the macrocycle and is coordinated by both pyrrole and two of four azomethine N atoms.[13]

Scheme 2



Mononuclear complexes with a planar macrocyclic environment based on derivatives of compound **1** were prepared by direct template syntheses starting from uranyl nitrate, 3,4-diethylpyrrole-2,5-dicarbaldehyde, and 1,2-diamino-4,5-dimethoxybenzene or 1,2-diaminoethane in the presence of the "proton sponge". In these complexes, the uranyl cation located in the cavity of the macrocycle is bound to all six N atoms.[14,15]

We found that the reaction of compounds **1** and **2** in acetonitrile in the presence of AcOH and the potential template agent, *viz.*, the polynuclear nickel complex $Ni_9(\mu_n\text{-}OOCBu^t)_{12}(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3$ (**3**), at room temperature afforded binuclear complex **5** (a dark-red compound). In complex **5**, two Ni atoms are linked to each other through two bridging acetate extra ligands. It should be noted that this complex can also be readily prepared by the reaction of compounds **3** and **4** in MeCN in the presence of AcOH (see Scheme 1).

According to the X-ray diffraction data, both Ni atoms in centrosymmetrical molecule **5** (Fig. 2) are located inside the macrocycle, each atom being coordinated by three N atoms (the Ni—N distances are 2.029, 2.034, and 1.937(2) Å). The coordination environment about the Ni atoms is completed to a distorted trigonal bipyramid with two O atoms of two acetate bridges (Ni—O, 2.021 and 2.010(2) Å). The interatomic Ni...Ni distance (2.5123(8) Å) is comparable with those found in other carboxylate binuclear "lanterns" of nickel.[16] The fused macrocyclic $C_{24}H_{16}N_6$ ligand in complex **5** is virtually planar. The angle between the mean plane passing through all non-hydrogen atoms of the ligand (the Ni atoms are located at a distance of 0.04 Å from this plane) and the plane of the acetate bridges is 89.5°. The maximum deviation of the atoms of the central macrocycle from its mean plane is ±0.09 Å. The maximum angle between the planar pyrrole and benzene rings is 5.8°.

Complex **5** is virtually insoluble in non-polar solvents and is moderately soluble in DMF, DMSO, and pyridine.

Each Ni^{II} atom has the spin-free electronic configuration d^8 and possesses two unpaired electrons. In this connection, molecule **5** can exist in the singlet, triplet, and quintet states. According to the results of quantum-chemical DFT calculations, the minima on the potential energy surface correspond to all three states, and their total energies differ by no more than 2 kcal mol^{-1}.

The measurements of the static magnetic susceptibility for complex **5** demonstrated that its effective magnetic moment increased from 0.569 to 2.614 μB as the temperature was raised from 2 to 301 K (Fig. 3). The experimental data were interpreted using the best fit method to fit the measured static magnetic susceptibilities (χ^e) to the theoretical values (χ^t) calculated per g-atom of the paramagnetic atoms. As a result, the following values were obtained: $S = 1$, $\langle g \rangle = 2.01$; $-2J = 360\ cm^{-1}$ (see Fig. 3). Hence, antiferromagnetic coupling occurs between two Ni^{II} ions in the complex under study, the first excited (triplet) level being located at a distance of 360 cm^{-1} (~1 kal mol^{-1}) from the ground (singlet) level, which is comparable with the values known for other nickel dimers with the "China-lantern" structure ($-2J = 260\ cm^{-1}$).[17]

Thus we prepared the first binuclear antiferromagnetic Ni^{II} complex in which the Ni...Ni frag-

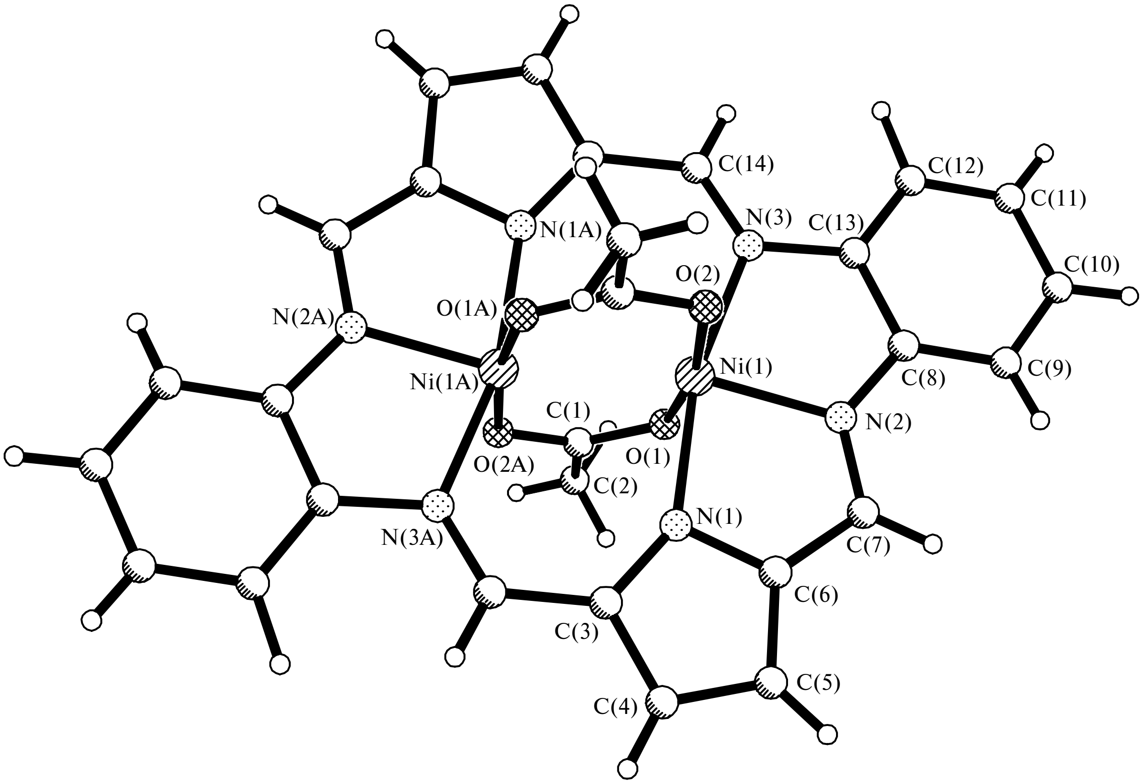


Fig. 2. Structure of the complex $C_{28}H_{22}N_6Ni_2O_4$ (**5**).

ment is located inside the completely conjugated macrocycle.

Experimental

Pyrrole-2,5-dicarbaldehyde (**1**)[18] and nickel pivalate $[Ni_9(HOOCBu^t)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCBu^t)_{12}]$ (**3**)[8] were prepared according to procedures described previously. The purified and dry solvents were used. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets in the frequency range of 392—4000 cm^{-1}. The diffusion reflection electronic spectra for polycrystalline samples and solutions were measured on a Specord M-400 spectrophotometer in the range of 200—900 nm. The measurements of the static magnetic susceptibility were carried out in the temperature range of 2—301 K on a MPMS-59 SQUID magnetometer in the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences. The mass spectra were obtained on a Finnigan MAT-50 instrument (direct inlet, EI, 70 eV). The ^{1}H NMR spectra were recorded on a Bruker DPX-300 spectrometer (300 MHz) with Me_4Si as the internal standard.

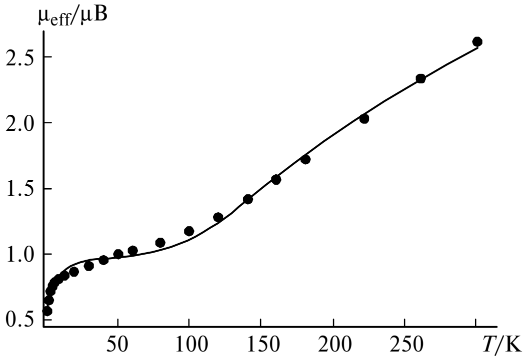


Fig. 3. Magnetic properties of the binuclear complex $C_{28}H_{22}N_6Ni_2O_4$ (**5**); the dotted and solid curves correspond to the theoretical and experimental dependences $\mu_{eff}(T)$, respectively.

Quantum-chemical calculations were carried out with the use of the PRIRODA program,[19,20] which employs the Gaussian-type basis sets for the solution of the Kohn—Sham equations and expansion of the electron density in the auxiliary basis set. The PBE functional,[10] which involves the electron density gradient, was used. The geometry was optimized using self-consistent application of gradient corrections without restrictions imposed on the molecular symmetry. The orbital basis sets included the contraction sets (5s1p)/[3s1p] for H, (11s5p2d)/[6s3p2d] for C, N, and O, and (17s13p8d)/[12s9p4d] for Ni. The type of the stationary points was determined based on analytical calculations of the second derivatives of the energy.

Schiff's bases 4. A solution of dialdehyde **1** (123 mg, 1 mmol) and *o*-phenylenediamine (**2**) (108 mg, 1 mmol) in anhydrous EtOH (50 mL) was refluxed for 1.5 h, cooled, concentrated to 5—7 mL, and kept at 5 °C for one day. The product crystallized as yellow-brown needles. The substance was filtered off, washed on a filter with cold EtOH, and dried *in vacuo*. Compound **4** was obtained in a yield of 158 mg (74%), m.p. 165—167 °C. Found (%): C, 67.68; H, 5.23; N, 19.83. $C_{12}H_{11}N_3O$. Calculated (%): C, 67.61, H, 5.16, N, 19.72.

^{1}H NMR (DMSO-d$_6$), δ: 12.50 (br.s, 1 H, H(11)); 9.60 (s, 1 H, H(1)); 8.55 (s, 1 H, H(4)); 7.17 (dd, 1 H, H(5), $J_{5,7}$ = 1.4 Hz, $J_{5,6}$ = 8.0 Hz); 7.07 (d, 1 H, H(2), $J_{2,3}$ = 4.0 Hz); 6.94 (ddd, 1 H, H(7), $J_{7,6}$ = 8.0 Hz, $J_{7,8}$ = 8.0 Hz, $J_{5,7}$ = 1.4 Hz); 6.80 (d, 1 H, H(3), $J_{2,3}$ = 4.0 Hz); 6.68 (dd, 1 H, H(8), $J_{8,6}$ = 1.4 Hz, $J_{7,8}$ = 8.0 Hz); 6.51 (ddd, 1 H, H(6), $J_{7,6}$ = 8.0 Hz, $J_{8,6}$ = 1.4 Hz, $J_{5,6}$ = 8.0 Hz); 5.60 (br.s, 2 H, H(9), H(10)). The assignment of the signals was made based on the NOE experiments (positive NOE was observed on the H(3) and H(5) nuclei on irradiation of the signal at δ 8.55) and using the 2D COSY 45 spectrum.

IR, ν/cm^{-1}: 3456 m, 3320 m, 2920 w, 2848 w, 2800 w, 1648 s, 1616 m, 1504 m, 1416 m, 1240 m, 1168 m, 1048 m, 952 w, 784 m. MS, *m/z* ($I_{\rm rel}$ (%)): 213 [M]$^+$ (83.8), 212 [M − H]$^+$ (53.3), 184 [M − HCO]$^+$ (41.9), 119 [M − C$_5$NOH$_4$]$^+$ (100). The electronic spectrum (a 0.0025 *M* solution in MeCN), $\lambda_{\rm max}$/nm (ε · 10^{-3}): 238 (6.84), 256 (6.96), 323 (9.26), 405 (5.72).

Synthesis of binuclear complex 5. ***A.*** AcOH (0.5 mL) was added to a solution of complex **3** (260 mg, 0.115 mmol), dialdehyde **1** (123 mg, 1 mmol), and *o*-phenylenediamine **2** (108 mg, 1 mmol) in MeCN (100 mL). The reaction mixture was kept for 24 h. The dark-red crystalline compound that formed was filtered off, washed with cold MeCN, dried *in vacuo*, and recrystallized from DMF. Solvate of **5** with DMF was obtained in a yield of 173 mg (45%).

B. A solution of complex **3** (260 mg, 0.115 mmol) and Schiff's base **4** (213 mg, 1 mmol) in MeCN (100 mL) was kept for 1 h. Then AcOH (0.5 mL) was added and the mixture was kept at ~20 °C for 24 h. Crystals of **5** were filtered off, washed with cold MeCN, and dried *in vacuo.* The product was recrystallized from DMF. Solvate of **5** with DMF was obtained in a yield of 204 mg (53%). Found (%): C, 52.96; H, 4.65; N, 14.62. $C_{34}H_{36}N_8O_6Ni_2$. Calculated (%): C, 52.99; H, 4.68; N, 14.55.

IR (KBr), ν/cm^{-1}: 2920 w, 1744 w, 1696 w, 1664 w, 1607 m, 1592 s, 1569 m, 1472 w, 1440 m, 1408 m, 1280 m, 1224 w, 1160 w, 1048 m, 944 w, 880 w, 752 m, 688 m, 624 w. The diffusion reflection electronic spectrum, $\lambda_{\rm max}$/nm: 235, 328, 455, 503, 568, 627, 673, 869.

The X-ray diffraction data for compound **4** were collected on a Siemens-P3/R3 diffractometer (λ-Mo-Kα, graphite monochromator, θ/2θ scanning technique, 2$\theta_{\rm max}$ = 50°). The structure was solved by the direct method using the SHELXS-86 program package[21] and refined by the least-squares method with anisotropic thermal parameters (isotropic thermal parameters for the H atoms) using the SHELXL-93 program package.[22]

The X-ray diffraction data for **5** · (Me$_2$NCHO)$_2$ were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ-Mo, graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, 2$\theta_{\rm max}$ = 60°) using a standard procedure.[23] The

Table 1. Crystallographic parameters of compounds **4** and **5** · (Me$_2$NCHO)$_2$

Compound	**4**	**5** · (Me$_2$NCHO)$_2$
Molecular formula	$C_{12}H_{11}N_3O$	$C_{34}H_{36}N_8Ni_2O_6$
Space group	*C*2/*c*	*P*2$_1$/*n*
a/Å	20.607(4)	14.2639(10)
b/Å	5.5090(10)	8.25599(6)
c/Å	19.962(4)	14.7057(11)
α/deg	90	90
β/deg	109.85(3)	109.673(2)
γ/deg	90	90
V/Å^3	2131.5(7)	1631.5(2)
Z	4	2
$\rho_{\rm calc}$/g cm^{-3}	1.329	1.568
μ/mm^{-1}	0.089	1.214
θ Scan range/deg	2.10—29.99	1.72—30.05
Number of independent reflections	1772	4539
R$_1$	0.0724	0.0495
w*R*$_2$	0.1424	0.1032

Table 2. Selected bond lengths (*d*) and bond angles (ω) for compound **4**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(5)	1.210(5)	C(1)—N(1)—C(4)	108.8(4)
N(1)—C(1)	1.371(5)	C(6)—N(2)—C(7)	120.2(4)
N(1)—C(4)	1.372(5)	N(1)—C(1)—C(2)	107.9(4)
N(2)—C(6)	1.268(5)	N(1)—C(1)—C(6)	122.5(4)
N(2)—C(7)	1.420(5)	C(2)—C(1)—C(6)	129.6(4)
N(3)—C(12)	1.363(6)	C(4)—C(3)—C(2)	107.8(4)
C(1)—C(6)	1.446(6)	N(1)—C(4)—C(3)	107.9(4)
C(3)—C(4)	1.379(6)	N(1)—C(4)—C(5)	122.7(4)
C(4)—C(5)	1.431(6)	O(1)—C(5)—C(4)	127.5(5)
C(7)—C(12)	1.416(6)	N(2)—C(6)—C(1)	121.6(4)
C(9)—C(10)	1.377(7)	C(8)—C(7)—C(12)	119.8(4)
		C(8)—C(7)—N(2)	125.8(4)
		C(12)—C(7)—N(2)	114.3(4)
		N(3)—C(12)—C(11)	122.4(5)
		N(3)—C(12)—C(7)	119.9(4)

Table 3. Selected bond lengths (*d*) and bond angles (ω) for complex **5** · (Me$_2$NCHO)$_2$

Bond	*d*/Å	Angle	ω/deg
Ni(1)—N(3)	1.937(2)	N(3)—Ni(1)—O(1)	96.63(9)
Ni(1)—O(1)	2.021(2)	N(3)—Ni(1)—O(2)*	92.64(9)
Ni(1)—N(1)	2.029(2)	O(1)—Ni(1)—N(1)	90.61(9)
Ni(1)—N(2)	2.034(2)	O(1)—Ni(1)—N(2)	91.61(9)
Ni(1)—Ni(1)*	2.5123(8)	O(2)*—Ni(1)—O(1)	170.10(8)
O(1)—C(1)	1.259(4)	O(2)*—Ni(1)—N(1)	87.18(9)
O(2)—C(1)	1.267(4)	O(2)*—Ni(1)—N(2)	92.84(9)
O(2)—Ni(1)*	2.010(2)	N(1)—Ni(1)—N(2)	166.12(10)
		N(3)—Ni(1)—N(1)	82.34(10)
		N(3)—Ni(1)—N(2)	83.79(10)
		N(3)—Ni(1)—Ni(1)*	166.30(8)
		O(1)—Ni(1)—Ni(1)*	87.36(6)
		O(2)*—Ni(1)—Ni(1)*	84.41(6)
		N(1)—Ni(1)—Ni(1)*	110.79(7)
		N(2)—Ni(1)—Ni(1)*	83.00(7)
		C(1)—O(1)—Ni(1)	119.8(2)
		C(1)—O(2)—Ni(1)*	123.6(2)
		C(3)—N(1)—Ni(1)	111.25(17)
		C(14)*—N(1)—Ni(1)	127.3(2)
		C(10)—N(2)—Ni(1)	107.31(19)
		C(13)—N(2)—Ni(1)	147.3(2)
		C(8)—N(3)—Ni(1)	115.95(19)
		C(9)—N(3)—Ni(1)	114.8(2)

* The atom is related to the initial atom by the transformation −*x*, −*y*, −*z*.

semiempirical absorption correction was applied.[24] The structure was solved by the direct method with the use of the SHELXS-97 program package[25] and refined by the full-matrix least-squares method with anisotropic thermal parameters (the positions of the H atoms were fixed with U_H = 0.08 Å^2) using the SHELXL-97 program package.[26] The atomic coordinates were deposited with the Cambridge Structural Database. The principal crystallographic data for complexes **4** and **5** · $(Me_2NCHO)_2$ are given in Table 1. The geometric parameters are listed in Tables 2 and 3, respectively.

Quantum-chemical calculations were carried out in the Interdepartmental Supercomputer Center on a Beta cluster. We thank V. M. Gryaznov and D. N. Laikov for helpful discussion, V. M. Nosova for help in recording the NMR spectra, and N. S. Kulikov for measuring the mass spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 99-03-32792, 99-03-32806, 00-15-97429, 01-03-32553, and 01-03-32537).

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Received July 11, 2001;
in revised form October 11, 2001